III.A.11 Development of Inexpensive Metal Alloy Electrodes for Cost-Competitive Solid Oxide Fuel Cells

Objectives

- Improve low temperature performance of the air electrode using catalyst infiltration technology developed at Lawrence Berkeley National Laboratory (LBNL). Three approaches are being evaluated for eventual transfer to industrial teams:
  - Dispersed catalyst infiltration on functional air electrodes (i.e. yttria-stablized zirconia/ lanthanum strontium manganate [YSZ/LSM]).
  - Continuous islands of nano-particle electrode coated on functional air electrodes.
  - Electronically connected nano-particle assembly coated onto porous ionically conductive network.
- Determine degradation rate of commercial air electrode structures with and without catalyst infiltration.
- Engineer performance of interconnect alloys through control of oxide scale growth and conductivity.
- Minimize Cr vaporization from stainless steel alloys.
- Transfer technology to industrial teams where appropriate.

Approach

- Develop low-cost metal salt infiltration technology to boost the performance of the air electrode, particularly at temperatures below 700ºC. The three approaches involve the use of simple catalyst impregnation to yield dispersed nano-particles, or a viscous catalyst precursor is vacuum impregnated into porous structures to yield a connected catalyst network. Vacuum impregnation can be accomplished with a porous electrolyte structure or an electrode/electrolyte (LSM/YSZ) network.

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- Measure the baseline performance and long-term stability of commercially produced air electrodes with and without infiltrated catalyst.
- Determine oxidation rates and Cr vaporization rates of commercial and specialty alloys under consideration for interconnect plates.
- Determine Cr vaporization coated alloys to determine quality of coating for minimization of Cr loss.
- Analyze Cr vaporization data to understand fundamental limits of coatings.

Accomplishments

- **Refinement of infiltration technology**: The LBNL infiltration technology has undergone continual refinement over the past 12 months, and we are now able to infiltrate a variety of complex microstructures including conventional air electrodes and porous electrolyte networks. In one approach the LBNL team infiltrates a dispersed catalyst using simple nitrate precursors. We are now collecting data on commercial air electrodes with and without infiltration to see the effect of instantaneous performance and long-term degradation. In another approach we impregnate a wide variety of microstructures with electrode catalysts using vacuum infiltration.
- **Successful determination of Cr vaporization rates for a number of coated and uncoated stainless steel alloys in humidified air**: The LBNL group has been very successful in determination of Cr vaporization from coated and uncoated stainless steel samples in humidified air, including coated samples provided from industrial developers such as Arcomac. The LBNL team has shown that although the Cr vaporization rate from uncoated ferritic steel is unacceptably high, the addition of a relatively simple coating as developed at LBNL can minimize this problem while simultaneously improving resistance to high temperature oxidation.
- **Demonstration of long-term suppression of Cr vaporization from coated ferritic steel**: The LBNL group developed simple, cost-effective coatings for ferritic steel that greatly improve stability towards high temperature oxidation, significantly decrease the Cr vaporization rate in humidified air, and maintain negligible Cr vaporization for at least 1,000 hours.

Future Directions

- **Determine long-term stability of infiltrated electrodes**: The LBNL group is presently conducting a study of baseline degradation of symmetrical LSM/YSZ/LSM and LSCF-CeO_2/YSZ/CeO_2-LSCF cells supplied to us by InDec/H.C. Starck. The LBNL group will determine the performance and degradation rate of the cells in air at 650°C for 1,000 hour tests, after which the electrodes will be infiltrated with appropriate catalysts and the test will be repeated. In this way the long-term stability of infiltrated electrodes can be separated from the long-term stability of the standard electrodes. The LBNL team will run tests on both electrode types, and with multiple infiltration species, and will do post-mortem studies on the electrode morphology.
- **Optimize infiltration technology**: The LBNL team is continually refining the technology for catalyst infiltration to accommodate a wide range of air electrode compositions and microstructures. This capability allows industrial teams to adapt the LBNL approach to their specific need. We will also use the results from the long-term stability studies to refine the composition and process of infiltration to ensure long-term performance improvement at reduced SOFC operating temperatures.
- **Use of analytical focused ion beam (FIB) and transmission electron microscopy (TEM) at the National Center for Electron Microscopy (NCEM)**: The LBNL team continues to develop infiltration technologies to assist the industrial teams in improving the low-temperature performance of the SOFC air electrode. A key aspect of this work is determination of the long-term benefit of this technology and elucidation of the mechanism(s) of degradation of the air electrode over time. Limited studies with NCEM are quite promising, and we hope to expand this effort with the ultimate goal of working with industrial teams on problems specific to their SOFC stacks.
- **Technology transfer**: The LBNL development of coating technology for ferritic steel interconnects is effectively complete and is ready for technology transfer. We anticipate that the LBNL infiltration technology will be ready for transfer to the industrial teams at the end of this 12-month period.

Introduction

Among the most challenging hurdles to the commercialization of SOFC technology is the need to manage cost such that SOFCs are competitive with entrenched power generation technologies. The LBNL group has long maintained that the key to a cost-effective SOFC solution is to develop systems operating in the 650 to 700°C range. A number of SECA industrial teams are now pursuing that goal as well. In order to achieve the 40,000-hour life needed for distributed generation, it is clear that stainless steel interconnects will have to be maintained at temperatures below 800°C. Since electrode kinetics (and electrolyte conductivity) are thermally activated, it is not a trivial task to maintain SOFC performance as the operating temperature is lowered. The LBNL group has developed several infiltration techniques whereby standard LSM electrodes can be modified to perform well at temperatures as low as 650°C. Electrode modification can be as simple as infiltrating a metal nitrate such as $Co(NO_3)_2$, involve a mixture of precursors to form a known electrocatalyst such as $Sm_{0.6}Sr_{0.4}CoO_{3-\delta}$ (SSC), or use the newly developed LBNL technique of vacuum impregnation of porous structures with connected nano-particle architectures. The LBNL group has also performed extensive investigations into high temperature corrosion of stainless steel alloys for interconnects, determined the Cr vaporization rates for steels in humidified air, and developed low-cost coating technologies that reduce Cr vaporization to negligible levels while simultaneously improving oxidation behavior. The LBNL team has initiated measurement of degradation rates of infiltrated and non-infiltrated air electrodes produced in-house and by commercial suppliers. We are also conducting FIB and TEM studies to aid in the elucidation of fundamental mechanisms for air electrode degradation and failure.

Approach

In order to achieve SECA commercialization targets, a number of SOFC developers are targeting reduced operating temperatures as a means of controlling cost. The LBNL effort is aligned with that goal through the use of electrode infiltration technology to boost the performance of the air electrode. The LBNL team has now expanded its infiltration technology to cover 3 basic types of infiltration: ***(1)*** *infiltration of simple metal nitrates to form dispersed nano-particle catalyst on the surface of functional air electrodes in order to boost low-temperature performance,* ***(2)*** *single-step infiltration into porous electrolyte networks to form a continuous nano-structured electrode surface, and* ***(3)*** *single-step infiltration of nano-particulate electrodes onto functional air electrodes such as YSZ-LSM*. The 1st infiltration technique is the simplest to implement and would not require significant change of SOFC processing by the industrial teams. It is clear that this technique results in a fairly dramatic boost in low-temperature air electrode performance. The LBNL group is now investigating the effects of infiltration on long-term performance and air electrode degradation. If the performance enhancement persists for several thousand hours, it may be possible to re-infiltrate the air electrode later in SOFC stack life by injection of metal nitrates into the air inlet. We are now conducting 1,000-hour tests on symmetric LSM-YSZ/YSZ/LSM-YSZ air electrodes provided to us by InDec, both infiltrated and non-infiltrated. The results of this testing will be used to make recommendations to the SECA vertical teams. The 2nd infiltration technique is quite different in concept from traditional SOFC design in that a porous electrolyte structure is co-fired with a dense electrolyte film at temperatures sufficient to fully densify the electrolyte. This technique allows the SOFC developer to use air electrode materials that are too reactive for conventional co-firing methodology. It also enables the use of porous metal supports and/or co-firing of electrolyte structures onto metal interconnects in reducing atmospheres; then the air electrode is infiltrated in a single-step and fired at low temperature in air. Such single-step infiltrated air electrodes have shown good performance and excellent stability for at least 500 hours at 700°C. The 3rd infiltration technique developed by the LBNL team represents a modification to the 2nd technique in that the single-step infiltration has been altered to allow infiltration of a highly connected nano-structure onto an existing air electrode network. For example, a nano-structured LSM feature can be added to the surface of a conventional LSM-YSZ air electrode. We initiated this work with in-house prepared LSM-YSZ air electrodes but will soon shift to commercial suppliers. This technique is more complex that the 1st infiltration technique but can also be adapted by the industrial teams, and may offer a higher performing and more stable structure.

Our work on high-temperature oxidation and Cr vaporization from coated and uncoated stainless steel is nearing completion. This has been a highly successful effort as we have shown that although Cr vaporization from stainless steel samples exposed to humidified air is unacceptably high, it can be reduced to negligible levels through the use of simple and inexpensive coating developed by the LBNL group. In the past 12 months we have also determined the Cr vaporization rate from coated and uncoated steel samples over a period of several weeks to ensure that the beneficial properties of the coatings are long lasting.

Results

The LBNL group fabricated a transpiration apparatus (Figure 1) and has used this equipment to successfully determine the Cr vaporization rate from a variety of Cr containing samples. As can be seen from the data illustrated in Figure 2, the rate of Cr loss is unacceptably high for uncoated ferritic steel, but is reduced by 2 orders of magnitude through the simple and inexpensive technique of aerosol spray-coating the steel surface with perovskites such as $La_{0.65}Sr_{0.3}MnO_{3-\gamma}$ (LSM), $La_{0.6}Sr_{0.3}Co_{0.8}Fe_{0.2}O_3MnO_{3-\gamma}$ (LSCF), and $MnCo_2O_4$ (MCO). Another remarkable benefit of such simple coating technology is a factor of 10 decrease in oxidation rate leading to a lower area specific resistance (ASR) for

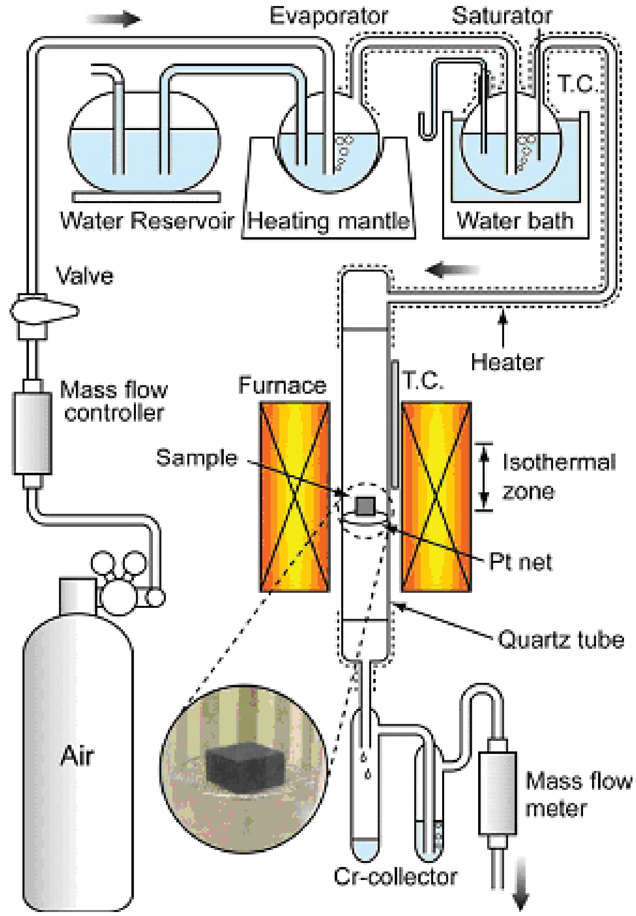

FIGURE 1. Chromium Transpiration Apparatus

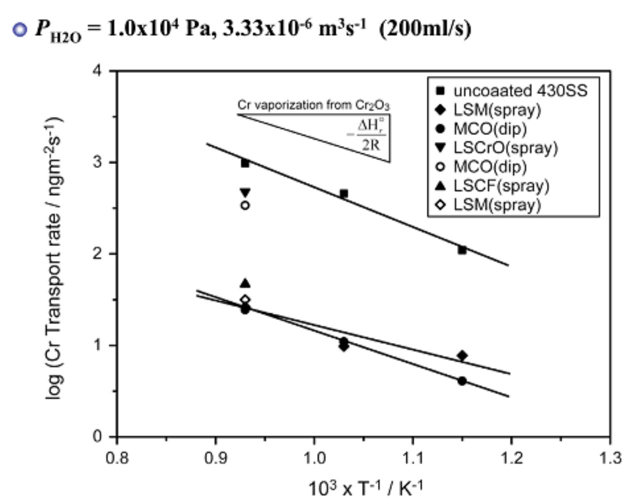

FIGURE 2. Cr transport Rate for Coated and Uncoated Steel Samples

the interconnect. The benefits of simple aerosol coating are therefore:

- Decrease oxidation rate >10x
- Decrease Cr vaporization by 10-100x
- Decreases spallation (thermal cycling)
- Decreases contact resistance

The LBNL team decided to examine the long-term effect of coatings on the Cr vaporization rates and the results of this study are shown in Figure 3. It is clear that coating the steel surface with a simple perovskite such as LSM lowers the Cr transpiration rate significantly and this benefit persists over time. This is certainly good news for SOFC developers, and the use of a LSM coating as an effective barrier for Cr transport provides an additional incentive for its use as a contact paste.

As described above, the LBNL group has developed several unique approaches to catalyst infiltration for high performance air electrodes. In Figure 4, LBNL researchers use an FIB to etch a trench into the infiltrated SOFC exposing a cross-section of the cell. Given that the infiltration technique produces a nano-particulate covering on the porous YSZ framework, a logical study would be the long-term stability of such a high surface area material at the cell operating temperature. As can be seen in Figure 5 the infiltrated structure exhibits excellent microstructural stability, at least for a period of 500 hours at the cell operating temperature. The LBNL team is also investigating the suitability of silver as an air electrode material and contact paste. The high mobility of Ag at operating temperatures above 600°C is a concern, but work at LBNL has shown that co-infiltration of LSM with Ag actually improves the performance of both materials as an air electrode and leads to good long-term stability (Figure 6). The LBNL group is also developing a technique for single-step infiltration of connected nano-structure on an existing air electrode such as conventional LSM-YSZ. The result of such an infiltration is shown in Figure 7; we have not yet tested the performance of such a structure. In the next performance period we will refine this technology to infiltrate connected nano-structures into commercially supplied air electrodes from InDec, and test their short-term and long-term performance.

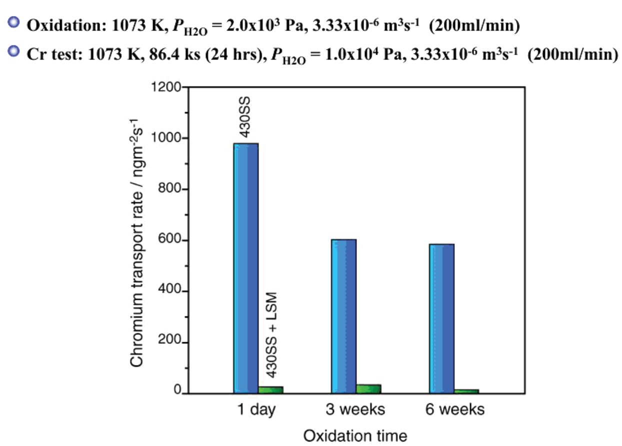

FIGURE 3. Chromium Transport Rate over Time for Coated and Uncoated Stainless Steel

FIGURE 4. FIB Trench Showing Cross-Section of Single-Step LSM Infiltrated Thin-Film SOFC

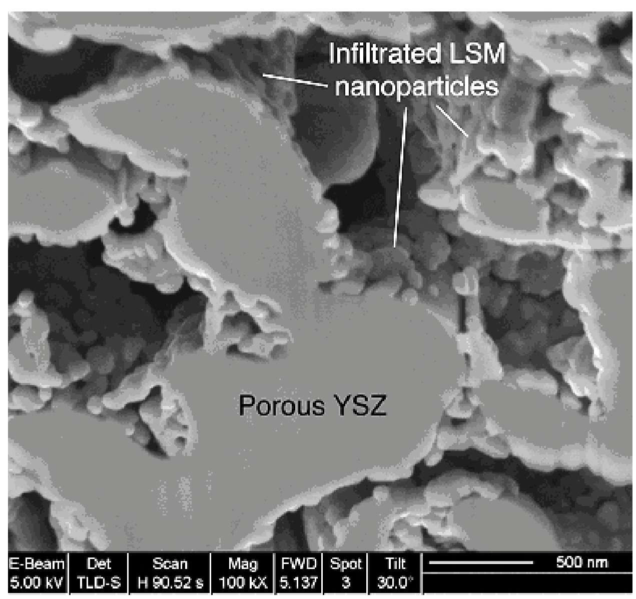

FIGURE 5. FIB Cross-Section Showing Intact Nano-Particle Superstructure on Porous YSZ Network after 500 hours Continuous Operation at 650°C

The LBNL group is monitoring the long-term stability of infiltrated electrodes by running 1,000-hour tests on commercially produced symmetric air electrode cells (i.e. LSM-YSZ/YSZ/LSM-YSZ) with and without infiltration of dispersed catalyst (type 1) and single-step connected nano-structures (type 3). In addition to determination of the voltage profile over time at constant current, we are doing pre- and post-mortem studies of the air electrode microstructure as well as analytical studies of the interfaces by FIB and TEM techniques. The LBNL team has initiated work with the user facilities of the National Center for Electron Microscopy (NCEM). Using the high resolution TEM we been able to observe changes in electrode structure after testing at the interface between the infiltrated catalyst and electrolyte. We will continue to expand the relationship between NCEM and the LBNL SOFC group with the aim of providing industrial teams with the ability to analyze their cell microstructures. We believe that the analysis of cells before and after testing will allow us to study regions with high probability of failure and aid us in providing solutions for the improvement of these regions. In Figure 8, a TEM image is shown of an LSM single-step infiltrated cathode. In Figure 9 an EDX spectroscopy line scan is highlighted which was taken between the backbone electrolyte particle and the catalytic LSM particle of an infiltrated cell that was operated continuously for 500 hours. A deficiency of oxygen that was not seen before testing was found at this boundary, suggesting that this is the "active" region of the electrode (see Figure 10). We are currently probing the "active" regions of infiltrated cells and have found some initial signs of a correlation between the surface energy between electrode components and electrode stability; we are optimistic that these studies will provide mechanistic information to further improve conventional

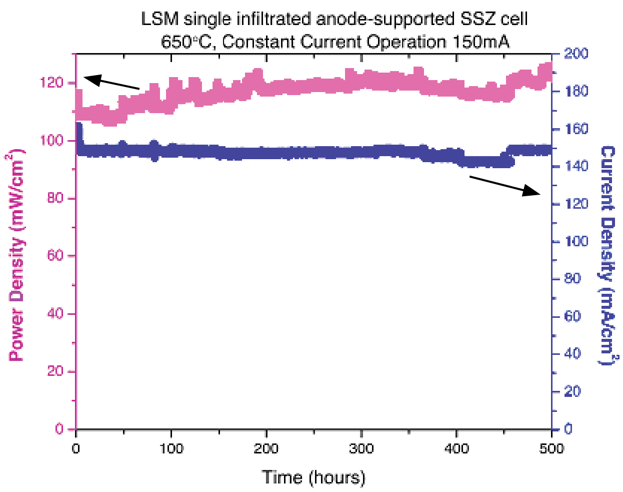

FIGURE 6. Performance and Long-Term Stability of SOFC Having Single-Step Infiltrated LSM Air Electrode

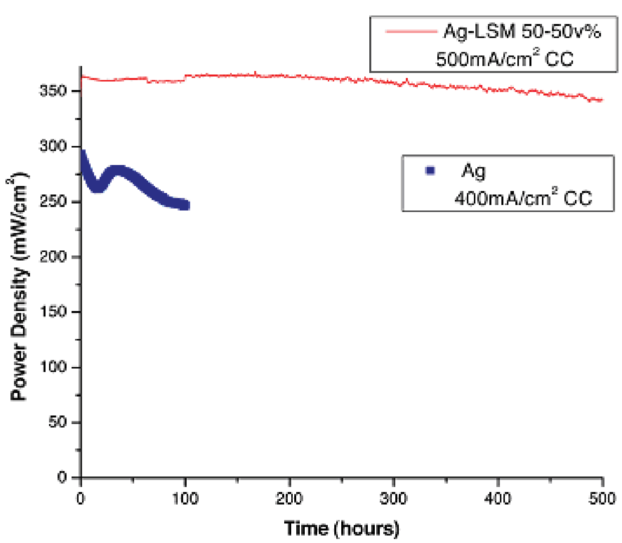

FIGURE 7. Improvement of Ag Electrode Performance through Co-Infiltration of Ag and LSM

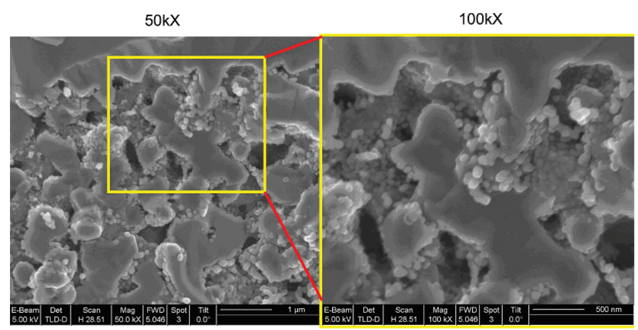

FIGURE 8. Single-Step Infiltration of LSM Nano-Particles into Conventional LSM-YSZ (1:1 wt%) Electrode; Sintered at 1300°C for 4 Hours

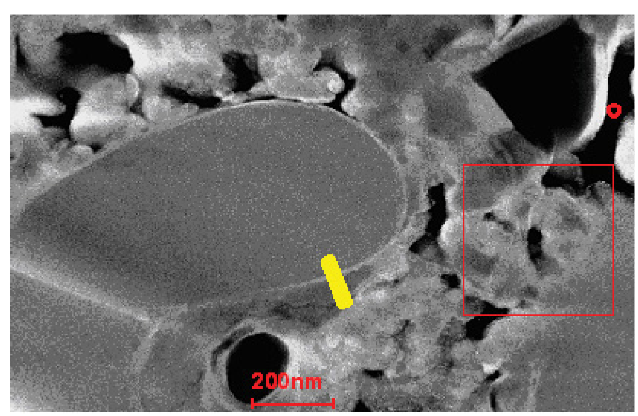

FIGURE 9. TEM of an LSM Single-Step Infiltrated Cathode (EDX line scan taken between backbone electrolyte particle and the catalytic LSM particle of an infiltrated cell that was operated continuously for 500 hours)

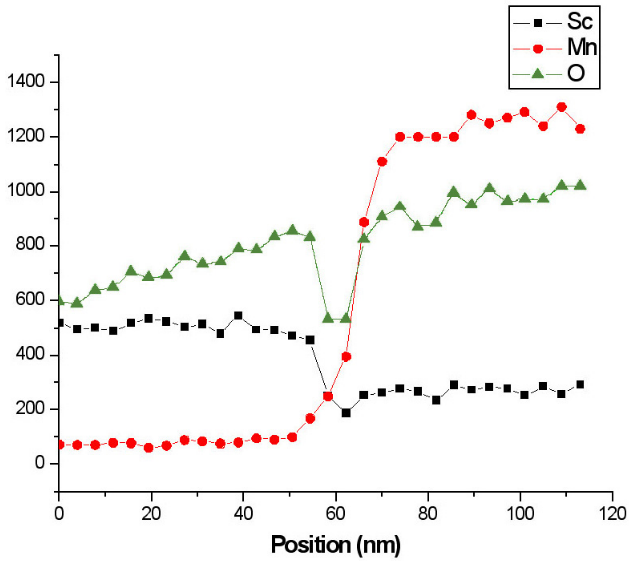

FIGURE 10. EDX Line Scan (indicated in Figure 9) Showing Oxygen Deficiency at the SSZ-LSM Boundary

and single-step infiltrated electrodes for long-term SOFC operation.

Conclusions

The use of simple and inexpensive coating technology developed at LBNL affords excellent protection of stainless steel components used in SOFC stacks against high temperature corrosion, spallation, and chromium vaporization in humidified air; such coating improve oxidation resistance by an order of magnitude and Cr vaporization rates are decreased by almost 2 orders of magnitude. The LBNL group has completed long-term testing of the coated steel samples and concluded that the beneficial effect of coatings in minimization of Cr vaporization is maintained, for at least 1,000 hours. The LBNL project has succeeded in refining its infiltration technology to allow infiltration of dispersed catalysts into conventional air electrodes to boost low temperature performance, or introduce an interconnected nano-particulate superstructure on the surface of conventional air electrodes. In all cases tested so far, the introduction of a dispersed catalyst improves air electrode performance at temperatures below 800°C; we are nearing completion of 1,000-hour tests and will report on the long-term stability shortly. Although single-step infiltrations of perovskite electrodes into porous YSZ have demonstrated excellent performance and stability (up to 500 hours of testing), we have not yet tested conventional electrodes with single-step infiltrated catalysts. The LBNL group has also initiated FIB and TEM analytical studies of air electrodes prior to and after long-term testing in an effort to elucidate the mechanism(s) for performance degradation over time; initial results are promising in that anomalies in oxygen concentration have been detected at the interface between the LSM electrode and YSZ electrolyte after 500 hours of SOFC operation.

FY 2006 Publications/Presentations

Papers

1. Michael C. Tucker, Hideto Kurokawa, Craig P. Jacobson, Lutgard C. De Jonghe and Steven J. Visco, "A Fundamental Study of Chromium Deposition on Solid Oxide Fuel Cell Cathode Materials" *Journal of Power Sources*; in press, corrected proof available online 10 March 2006.

2. Michael C. Tucker, Craig P. Jacobson, Lutgard C. De Jonghe and Steven J. Visco, "A Braze System for Sealing Metal-Supported Solid Oxide Fuel Cells," *Journal of Power Sources*, in press, corrected proof available online 31 March 2006.

Presentations

1. "Enhanced Low Temperature Electrode Performance by Infiltration," Craig Jacobson, Xuan Chen, Tal Sholklapper, Steve Visco, Lutgard De Jonghe American Ceramic Society 30th International Conference and Exposition on Advanced Ceramics and Composites, Cocoa Beach, FL, January 23-27, 2006.

2. "Metal-Supported Thin Film Zirconia and Ceria SOFCs," Mike Tucker Craig Jacobson, Jason Nicholas, Steve Visco, Lutgard De Jonghe; American Cermaic Society 30th International Conference and Exposition on Advanced Ceramics and Composites, Cocoa Beach, FL, January 23-27, 2006.

3. "Interconnect Performance in SOFC Environments," Craig Jacobson, Hideto Kurokawa, Mike Tucker, Peggy Hou, Steve Visco, Lutgard De Jonghe 2006 TMS Annual Meeting, March 14th 2006, San Antonio, Texas.

Special Recognitions & Awards/Patents Issued

1. U.S. Patent No. 6,979,511; Steven J Visco; Craig Jacobson; Lutgard C. DeJonghe, *"Structures and fabrication techniques for solid state electrochemical devices"* issued December 27, 2005.

2. U.S. Patent No. 6,921,557; Craig Jacobson, Steven J Visco, Lutgard C. DeJonghe; *"Process for making dense thin films"* issued July 26, 2005.